PHOTOCATALYTIC REDUCTION OF CO_2 WITH SOLVENT ON ALUMINA SUPPORTED WITH TIO_2

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A thesis submitted to the Faculty of Chemical and Natural Resources Engineering in partial fulfillment of the requirement for the Degree of Bachelor of Engineering in Chemical Engineering (Gas Technology)

Faculty of Chemical and Natural Resources Engineering
Universiti Malaysia Pahang

FEBRUARY 2013

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ABSTRACT

Carbon dioxide accounts for the largest share of the world's greenhouse gas emissions. There is a growing need to mitigate CO_2 emissions. One of the strategies to mitigate CO_2 emissions is using CO_2 as a raw material in chemical processes. Reactions involving CO_2 typically required high energy input and energy substrate. One of the best routes to reduce CO_2 is to transform it to hydrocarbons via photo reduction method. Before that, the methods of preparing catalyst such as sol-gel method and hydrothermal method were studied. Addition of metal oxide such as alumina to TiO_2 will changed the distribution of electrons and they prevented the electron hole recombination, thereby enhancing the photo catalytic efficiency in production of methanol. Therefore, hydrothermal method is expected give higher performances of catalyst compared to Sol Gel method. In addition, the effect of catalyst dosage for photo reduction process will be studied. The variety dosages of Al_2O_3-TiO_2 catalyst used are0.5 g, 1.0 g, 1.5g and 2.0 g. The period of reaction for each catalyst dosage is 6 hours which the sample is withdrawn for every 1 hour. Lastly, the sample of methanol is analysed using HPLC.

PENGURANGAN FOTOPEMANGKIN CO_2 DENGAN PELARUT TERHADAP ALUMINA YANG DISOKONG OLEH TIO_2

ABSTRAK

Karbon dioksida merupakan penyumbang terbesar kepada pelepasan gas rumah hijau di dunia. Terdapat satu keperluan yang semakin meningkat untuk mengurangkan pelepasan CO_2. Salah satu strategi untuk mengurangkan pelepasan CO_2ialah dengan menggunakan CO_2 sebagai bahan mentah dalam proses kimia. Reaksi yang melibatkan tenaga CO_2 biasanya memerlukan tenaga input yang tinggi dan tenaga substrat. Salah satu jalan terbaik untuk mengurangkan CO_2 adalah dengan mengubahnya kepada hidrokarbon melalui kaedah proses pengurangan foto dengan pemangkin. Sebelum itu, kaedah penyediaan pemangkin seperti kaedah sol-gel dan kaedah hidroterma perlu dikaji terlebih dahulu. Penambahan logam oksida seperti alumina terhadap TiO_2 akan mengubah pemindahan elektron dan menghalang penggabunganelektron lubang semula, dengan itu ia akan meningkatkan kecekapan foto pemangkin dalam pengeluaran metanol. Oleh itu, kaedah hidroterma dijangka memberi persembahan pemangkin yang lebih tinggi berbanding dengan kaedah sol-gel. Di samping itu, kesan dos pemangkin terhadap proses pengurangan foto juga dikaji. Pelbagai berat dos pemangkin Al_2O_3-TiO_2 yang digunakan adalah 0.5 g, 1.0 g, 1.5g dan 2.0 g. Tempoh tindak balas bagi setiap dos pemangkin adalah 6 jam dan sampel diambil pada setiap 1 jam. Akhir sekali, sampel metanol dianalisis menggunakan HPLC.

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LIST OF SYMBOLS

°	degree
° C	degree celcius
Psi	pascal
e^-	negative electron
eV	electron volt
g	gram
h	hour
h^+	positve electron
M	Molarity
mA	mili ampere
mL	mili litre
ng/ μL	nano gram per micro litre

LIST OF ABBREVIATIONS

TiO_2	Titanium dioxide
Al_2O_3	Aluminium oxide
HPLC	High pressure liquid chromatography
CH_3OH	Methanol
H_2SO_4	Sulphuric acid
H_2O	Water
OH	Hydroxide
$Ti(OC_3H_7)_4$	Titanium-tetra-isopropoxide
H	Hydrogen
CO_2	Carbon Dioxide
NAOH	Sodium Hydroxide
C	Carbon
BET	Brunaeur-Emmett-Tellar
XRD	X-Ray diffraction
C_2H_5OH	Ethanol

CHAPTER ONE

INTRODUCTION

1.0 Overview

According to the intergovernmental Panel on Climate Change (IPCC), (2001), the earth's surface temperature has risen by approximately 0.60 K in the past century, which particularly significant warning over the past two decades (Phairat Usubharatana et. al., 2006). After study, it is proved that the main contributor to this phenomenon is CO_2 emission from fuel combustion especially. The higher concentration of CO_2 is increasing in the atmosphere. This heating effect on earth produced in this way will caused the greenhouse effect and global warming. The excessive heating on earth and its atmosphere can have effect on our climate, which will affect us and all living beings. The climate will change into gradually hot. When temperature keeps rising all over the years, this will also affect the human health. It will approach to many diseases like skin cancer and badly fever (Phairat Usubharatana et. al., 2006).

A great deal of effort has been expanded to reduce CO_2 emissions from the industries where the largest percentages of fossil fuels are used. Some of the strategies to reduce CO_2 emission are energy conservation, carbon capture and storage and using CO_2 as a raw material in chemical processes. But some of them are very costly, with significant energy required for CO_2 stripping and solvent regeneration. However, there is one potential technology was introduced in reducing CO_2 recently. The technology of process called photo catalytic method.

Photo catalytic technology process can be applied for CO_2 removal with simultaneously converting CO_2 to marketable products such as methanol. Another potential feature of the photo catalytic reduction of CO_2 is the use of solar energy for the reaction or another ultraviolet light source can be used (Rajasalakshmi, 2011).

In this study, the photo catalytic reduction process using semiconductor materials to promote reaction in the presences of UV light was used. If we examine the thermodynamics of CO_2 reduction, we can find that the direct one-electron reduction of CO_2 to CO_2^- is a very energy intensive. So, the used of semiconductor such as aluminium oxide promoted with titanium dioxide as a catalyst for photo catalytic reduction process has received a lot of attention for several reasons. So that, their absorption properties can be tunes to capture visible light and their reduction potentials can be tuned to match the potential required of CO_2 reduction (David and Etsuko, n.d).

The main product from photo catalytic reduction of CO_2 is methanol. Methanol is light, volatile, colourless, flammable liquid with a distinctive odour very similar. At room temperature, it is a polar liquid, and is used as an antifreeze, solvent, fuel, and as a denaturant for ethanol. It is also used for producing biodiesel via Trans esterification reaction. Methanol is a common laboratory solvent. It is especially useful for HPLC, UV/VIS spectroscopy and LCMS due to its low UV cut off. The largest use of methanol by far is in making other chemicals. About 40 % of methanol is converted to formaldehyde and from there into products as diverse as plastics, plywood, paints, explosive, and permanent press textiles. Methanol is also used, as the primary fuel ingredient since the late 1940s, in the power plants for radio control, control line and free flight airplanes.

1.1 Problem Statement

Due to an increasing atmospheric CO_2 level in environment, an urgent need for the discovery of carbon neutral sources of energy to avoid the consequences of global warming should be find. An attractive possibility is to use CO_2 captured from industrial emissions as a feedstock for the production of useful fuels and precursors such as methanol.

An active field of research to achieve this goal is the development of catalysts that capable of harnessing solar energy for use in artificial photosynthetic processes for CO_2 reduction. Transition metal complexes are excellent substances, and it has already been shown that they can be used to reduce CO_2 with high quantum efficiency. In this study, alumina promote with titanium oxides catalyst was used in order to obey the fact that transition metal is a good catalyst to absorb the visible light and trap CO_2.

Photo catalysis is the main process for this case. It makes use of semiconductors to promote reactions in the presence of light radiation. Unlike metals, which have a continuum of electronic states, semiconductors exhibit a void energy region, or band gap, that extends from the top of the filled valance band to the bottom of the vacant conduction band. It is occur when it exposed to the light of radiation.

1.2 Research Objectives.

This objectives of this research are:

- To identify the best method for preparing of Al_2O_3 / TiO_2 catalyst
- To study the effect of catalyst dosages on photo reduction process.

1.3 Research Scopes

- In order to achieve objectives, a few activities were carried out. Al_2O_3 / TiO_2 catalyst was prepared using two different methods which are hydrothermal and sol-gel method. These methods includes various techniques of crystallizing substances at high temperature and high pressures aqueous solution. In hydrothermal method, preparation of catalyst was performed in an apparatus consisting of a steel pressure vessel called autoclave, in which a nutrient was supplied along with water at 121 ºC.

- Sol-gel was another method that can be used besides hydrothermal. It involves the formation of sol followed by formation of a gel, typically uses either colloidal dispersion material at 70 ºC.

- The parameter such as dosages of catalyst was varied in order to investigate the effect of the amount of catalyst that used in photo reduction process. The variety of catalyst dosage were performed from 0.50, 1.0, 1.5 and 2.0 g for each prepared catalyst.

1.4 Organization of the Thesis

This thesis consists of five chapters which are introduction, literature review, methodology, results and discussion and also conclusion. The first chapter is introduction which deals with describing information about photo catalytic process and the main problem due to the high concentration of CO_2 in atmosphere. The problem statement, research objectives and scope of the research was also represented.

Chapter two deepens on literature review that supported the photo catalytic reaction process. Some of mechanism of reaction equations also was stated.

Chapter three is research methodology which reviews about procedure to complete the experiment. The procedure involves such as method in preparing catalyst and photo catalytic reaction process.

Chapter four is where result is tabulated and explanations about discussion. There are two figures involved to support the results.

Chapter five is the last chapter that conclude overall about the thesis. Some recommendations regarding the experiment also are stated.

CHAPTER TWO

LITERATURE REVIEW

2.0 Introduction

A hot button topic for the last decade has been the effects of CO_2 on the environment. The CO_2 accounts for the largest share of the world's greenhouse gas emissions due to its concentration in Earth's atmosphere has increased during the past century. There is a growing need to mitigate CO_2 emissions. Some of the strategies to mitigate CO_2 emissions are energy conservation, carbon capture and storage and using CO_2 as raw material in chemical processes. Reactions involving CO_2 typically require energy input and/or a high energy substrate. The energy source should be provided without producing more CO_2, such as solar energy. One of the best routes to remedy CO_2 is to transform it to hydrocarbons such as methanol via photo reduction process. There by, solar energy is transformed and stored as chemical energy (Rajalakshmi, n.d).

The emission of CO_2 into the atmosphere, released mainly by the burning of fossil fuels is one of the most serious problems with regard to the greenhouse effect (Anpo, 1995). All human activity generates about 37 billion tons (37 Gt) of CO_2 emissions each year, with about 30 Gt of this coming from energy-related emissions. Total emissions were less than 25 Gt twenty years ago, and under business as usual scenarios, emissions are projected to rise to over 50 Gt twenty years from now. Burning 1 tonne of carbon in fossil fuels releases more than 3.50 tonnes of CO_2 (Maginn, 2010). The Earth's surface temperature has risen by approximately 0.60 K in the past century, with particularly significant warming trends over the past two decades. Hence CO_2 reduction/management (capture, storage & sequestration) has become a key issue in controlling global warming. **Figure 2.1** shows the level of CO_2 concentration in atmosphere from July 1990 – 2011.

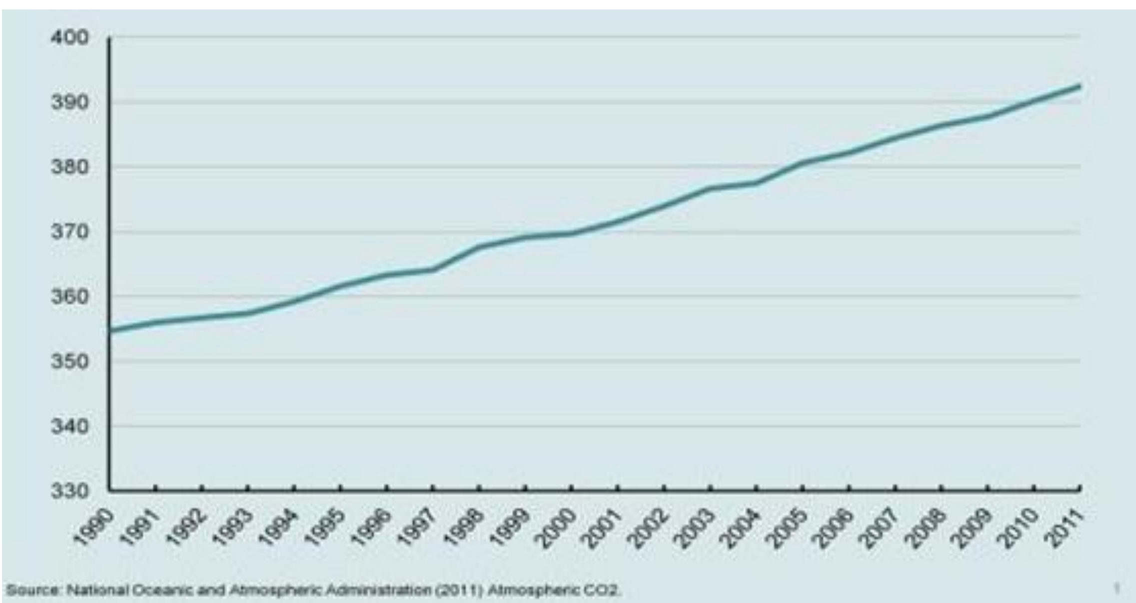

Figure 2.1 : CO_2 concentration in atmosphere, July 1990 – 2011 (Maginn, 2010).

Level of CO_2 concentration in atmosphere was increased from year 1990 until 2011. This is due to the effect of transportation or industrial sector that involve in releases CO_2 on atmosphere. The increasing level of CO_2 in atmosphere cause bad effects to environments such as human health, aquatic life and also flora and fauna (Murgatroyd, 2001).

CO_2 is the linear molecule consists of a carbon atom that is doubly bonded to two oxygen atoms, O=C=O. Although CO_2 mainly consists in the gaseous form, it also has a solid and a liquid form. It can only be solid when temperatures are below -78 ^{o}C. Liquid CO_2 mainly exists when CO_2 is dissolved in water. CO_2 is only water-soluble, when pressure is maintained (Alexandra Juniper, 2001).

There are two properties of CO_2 which can be divided into physical and chemical properties. The physical properties of CO_2 are its gas has a slightly odour and colourless and heavier than air. It can freezes at -78.5 °C to form CO_2 snow and the density is 1032 kg/m^3. Whereas for chemical properties of CO_2, it has vapour pressure about 58.5 bar and latent heat of vaporization at 571.08 kJ/kg. Although CO_2 is non-toxic and bacteriostatic, but it still can harm to the environment that cause greenhouse effect (Murgatroyd, 2001).

2.1 Photocatalyst Reduction of Carbon Dioxide (CO_2)

Photo-catalysis in simple meaning is acceleration of photoreaction in the presences of catalyst. It makes use of semiconductors like titanium dioxide (TiO_2) to promote reactions in the presence of light radiation. Different to metals, which have a continuum of electronic states, semi-conductor exhibit a void energy region, or band gap, that extends from the top of the filled valance band to the bottom of the vacant conduction band when exposed to light radiation (Phairat Usubharatana et. al., 2006). In photo-generated catalysis also, the photo-catalytic activity (PCA) depends on the ability of the catalyst to create electron-hole pairs. The catalyst will generate free radicals such as OH^- to able undergoes secondary reaction (Phairat Usubharatana et. al., 2006).

Due to increasingly level of CO_2 in atmosphere, the greenhouse effect problem is obvious. Photo-reduction of CO_2 then become in the future an alternative solution not only for environmental problems caused by CO_2 emission, but also for finding ways to maintain hydrocarbon resources which now on are being dominated by fuel and natural gas (Slamet et. al., 2009). The CO_2 reduction process is thermodynamically uphill as illustrated by its standard free energy of formation ($\Delta G° = 394.359$ kJ/mol) (Indrakanti, 2009). Economical CO_2 fixation is possible only if renewable energy, such as solar energy, is used as the energy source. Equally difficult is the reduction splitting of NaOH to yield hydrogen and hence requires similar combination of activation steps. The most ideal and desirable process would then be the simultaneous reduction of CO_2 and NaOH to yield methanol (Indrakanti, 2009).

According to Saeki et. al., (n.d) who studied the electrochemical reduction of CO_2 under various pressures galvano statically at 200 mA/cm^2 in a methanol medium. The results show that the current efficiency (ratio of the electrochemical equivalent current density for a specific reaction to the total applied current density) of CO_2 reduction increased from 23 % at 1 atm (0.10 MPa) to 92 % at 20 atm (2 MPa). High pressure enhances the reaction, as reflected in the increased equivalent current density. This effect can be applied to photo-catalysis with the same amount of energy supplied to the identical system. The difference between electrochemical reduction and photo-catalysis is the source of electrons. Electrons from the electrochemical process are supplied by an applied current; electrons for photo-catalysis are supplied by a semiconductor exposed to light radiation (Saeki et. al., n.d).

In photo-catalytic reduction, TiO_2 can affect the efficiency and selectivity of the methanol produced. The most crucial problem is a low quantum yield in the photo-catalysis process due to electron and positive hole recombination. In order to increases yield, TiO_2 must be modified by using dopants of metal. In CO_2 photo-reduction, Yamashita et. al., (n.d) reported that the addition of copper could improve the efficiency and selectivity to produce methanol.

Since CO_2 is a relatively inert and stable compound, its reduction is quite challenging and difficult to do. The reduction involves conversion and removal methods that require high-energy input which meant high temperature and pressure conditions. Conversely, photo catalysis occurs under relatively mild conditions with lower energy input when the reaction is activated by solar energy or other light resources (Phairat

Usubharatana et. al., 2006). Actually solar energy has the advantages which are; it can be used continuously and readily can be power supply.

The relationship of using TiO_2 as a semiconductor catalyst promotes the reaction in the presences of light sources. The function of TiO_2 is to create the band gap or void energy region. The band gap is characteristic for the electronic structure of a semiconductor and is defined as the energy interval (ΔE_g) between the valence band (VB) and the conduction band (CB). VB is defined as the highest energy band in which all energy levels are occupied by electrons, whereas CB is the lowest energy band without electrons. According to the band gap model, VB electrons are transferred to the CB when the semiconductor is illuminated with photons having energy content equal to or higher than the band gap, creating electron–hole pairs (Demeestere et. al., 2007).

Actually the UV light sources emit the electron that have energy equal or greater than band gap in order to transfer the electron to the band gap due to make it chemical reactions in the photo catalytic process possible. Migration of electron and holes to the semiconductor surfaces is followed by transfer of photo induced electron to absorb the solvent (Phairat Usubharatana et. al., 2006). The electron process will be more efficient if the species are absorbed on the surface. At the surface, the semiconductor, TiO_2 can donate electron to acceptor by using pathway A. The hole can migrate to the surface where they can combine with electron from donor species in pathway B. **Figure 2.2** shows the mechanism of photo excitation process.

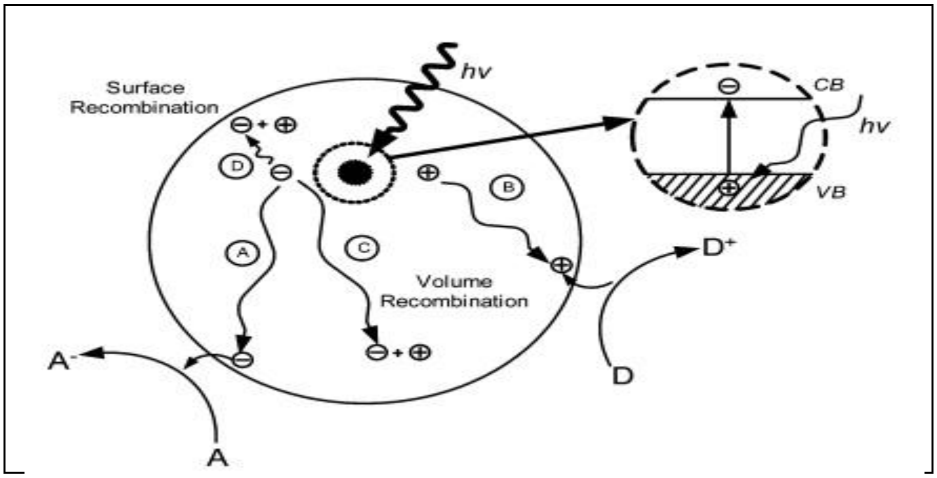

Figure 2.2: Photo excitation in solid followed by de-excitation (Seng et. al., 2006)

The first step involving photo catalytic splitting of solvent such as water follows the well-accepted elementary steps as shown in Eqs. (2.1) to (2.6).

$$TiO_2 + hv \longrightarrow e^- + h^+ \quad (2.1)$$

$$H_2O \longrightarrow H^+ + OH^- \quad (2.2)$$

$$H^+ + e^- \longrightarrow H. \quad (2.3)$$

$$OH^- + h^+ \longrightarrow OH. \quad (2.4)$$

$$2OH. \longrightarrow H_2O_2 + h^+ \longrightarrow O_2^- + 2H^+ \quad (2.5)$$

$$O_2^- + h^+ \longrightarrow O_2 \quad (2.6)$$

The second step for activation and reduction of CO_2 could then follow different pathways. Anpo et. al., (n.d) have identified ESR signals due to C and H atoms, CH_3 radical and Ti^{3+} ion on powdered titania catalyst in presence of CO_2 and water at 77 K.

Accordingly, the following pathway Eqs. (2.7)-(2.13) involving the formation of active surface carbon and its reaction with H and OH radicals (Anpo et. al., n.d).

$$CO_2 + e^- \longrightarrow {}^{\bullet}CO_2^- \tag{2.7}$$

$$ {}^{\bullet}CO_2^- + {}^{\bullet}H \longrightarrow CO + OH^- \tag{2.8}$$

$$CO + e^- \longrightarrow CO^- \tag{2.9}$$

$$ {}^{\bullet}CO- + {}^{\bullet}H \longrightarrow {}^{\bullet}C + {}^{\bullet}OH^- \tag{2.10}$$

$$ {}^{\bullet}C + {}^{\bullet}H^+ + e^- \longrightarrow {}^{\bullet}CH \longrightarrow {}^{\bullet}CH_2 \longrightarrow {}^{\bullet}CH_3 \tag{2.11}$$

$$ {}^{\bullet}CH_3 + {}^{\bullet}H^+ + e^- \longrightarrow {}^{\bullet}CH_4 \tag{2.12}$$

$$ {}^{\bullet}CH_3 + {}^{\bullet}OH \longrightarrow CH_3OH \tag{2.13}$$

Observation by Yang et.al. (n.d), on the formation of carbon residues and ESR evidence on hydrogen, methyl and methoxy radicals and $CO3^-$ anion radicals by Dimitrijevic et.al (n.d). on titania surface during CO_2 photo catalytic lend credence to this mechanism. Besides, CO as one of the reduction products has been reported on titania and metal supported titania. Methanol is formed through surface methoxy species and its further reduction results in methane production.

The rate of a photo catalytic reaction especially depends on the type of the photo catalytic semiconductor and on the light radiation that it used in its initiation (Koci et. al., 2008). **Table 2.1** shows the different of semi-conductor has different band of gap energy consume in photo catalytic reduction.

Table 2.1: Varies of semiconductor of photocatalyst with their band gap energy **(**Kabra et. al., n.d)

Photo catalyst	Band gap energy (eV)	Photo catalyst	Band gap energy
Si	1.1	TiO_2 rutile	3.02
Wse$_2$	1.2	Fe_2O_3	3.1
R-Fe_2O_3	2.2	TiO_2anatase	3.23
CdS	2.4	ZnO	3.2
V_2O_5	2.7	$SrTiO_3$	3.4
WO_3	2.8	SnO_2	3.5
SiC	3.0	ZnS	3.7

ZnS has the highest band gap energy which is 3.7 eV compared to TiO_2 rutile and anatase. In photo catalytic reduction process, electron is being emitted due to the heat sources from UV light. H^+ from hydrogen molecules will combine with CO_2 to produce the methanol.

The generation of electron-hole pairs (e--h+) and its reverse process are shown in Eqs. (2.14) and (2.15), respectively where hV is the photon energy, e- represents a conduction band electron, and h^+ represents a hole in the valence band. The mechanism process involves by simple equation is shown in Eqs. (2.14) and (2.15).

$$\text{Photo catalyst} \longrightarrow e^- + h^+ \tag{2.14}$$

$$e^- + h^+ \longrightarrow \text{heat} \tag{2.15}$$